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V. S. Nikitin, T. N. Ostanina,
V. M. Rudoy, A. S. Farlenkov
Ural Federal University, 19, Mira str.,
Ekaterinburg, Russia,
E-mail: nikitin-viachieslav@mail.ru

Dynamics of electrocrystallization of dendritic zinc deposits in galvanostatic and potentiostatic modes

In the work the dynamics of growth of zinc dendritic deposits in the galvanostatic and potentiostatic modes from an electrolyte containing 0.3 mol/L of ZnO, and 4 mol/L of NaOH has been studied. It has been shown that in galvanostatic conditions decrease in the elongation rate of dendrites and change in the deposit structure from dendritic to compact accompanied by increasing density and decreasing through-thickness porosity are observed. In potentiostatic conditions dendrites grow at a constant rate and the structure of the deposit varies little. The results have been confirmed by electron microscopic studies of morphology of zinc particles.

Key Words: electrocrystallization; zinc; dendritic, electrochemistry.

Introduction

The electrolytic zinc deposits possess unique dendritic structure and high purity, and powders derived from them are used in various technical fields (manufacture of batteries and zinc-rich composite materials). The structural properties of these deposits produced by electrolysis of aqueous solutions undergo changes after removal from the electrode, but the morphology of the particles, which is laid at the stage of electrolysis, remains unchanged after processing operations of the future powder [1]. In this connection, to obtain electrolytic powders with desired properties it is necessary to know how the deposition modes affect structural properties (density, porosity, surface area, etc.) of the deposit directly during its formation *in situ* [2]. By varying the conditions of electrodeposition (mode, preset current or potential, concentration of discharging ions, surfactant additives) it is possible to produce powders of various structure.

The aim of the present work is to study the dynamics of the electrocrystallisation process and the properties of dendritic zinc deposits in conditions of setting direct current and constant potential.

Experimental technique

To study the dynamics of dendritic zinc deposits an installation allowing simultaneous registering the change in potential (or current), video recording deposit growth and fixing the amount of hydrogen released has been used. A 1 cm high pin cathode made of zinc wire with a diameter of 2 mm has been brought to a center of a cylindrical cell. On the edge of the cell a ring zinc anode has been disposed. Polarization measurements were performed using Solartron potentiostat 1280C. The potential has been measured in respect to the zinc reference electrode. The deposits have been prepared from zincate electrolyte containing 0.3 mol/L of ZnO, and 4 mol/L of NaOH, when setting direct current and constant potential. Polarizing current has exceeded the value of the limiting diffusion current in 6 times. When using potentiostatic conditions a constant overvoltage equal to –0.38 V has been maintained, this corresponded to the level of diffusion limitations galvanostatic electrolysis. Analysis of video record of the deposit growth process has allowed to establish the dependence of the thickness of the dendritic deposit layer from time and to calculate the overall deposit volume. According to volumetric measurements current efficiency of zinc and hydrogen has been determined, that has allowed calculating the mass change of the deposit in the electrodeposition process. Microstructural studies of deposits have been carried out on Mira 3 LMU scanning electron microscope in IHTE laboratory of UB of the RAS.

Results and discussions

Under galvanostatic conditions due to the high current density the rate of ad-atoms formation is high. Delivery of discharging ions to surfaces with small radii (irregularities and crystallites) is facilitated due to the realization of mechanism of the spherical diffusion, so the discharge of zinc ions occurs mainly on high points, and then on tops of dendrites branches. There is a lengthening of existing and originating of new branches. Due to formation of plurality of branches the surface on which the discharge of metal ions takes place increases, and the current density decreases. At that the rate of dendrites elongation over time (Fig. 1) and the absolute value of the overvoltage (Fig. 2, curve 1) is gradually reduced. After recession of diffusion limitations mechanism of the process changes, particles on the deposits outer surface thicken. After 35 minutes of electrolysis the rate of dendrite growth falls distinctly, and the absolute value of the overvoltage reaches a constant value (Fig. 2, curve 1).

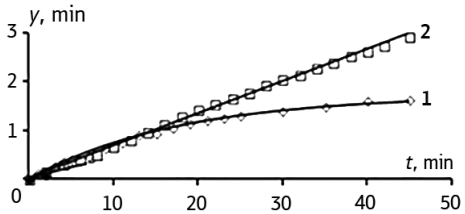

Fig. 1. Change the length of zinc dendrites in time in galvanostatic (1) and potentiostatic (2) modes

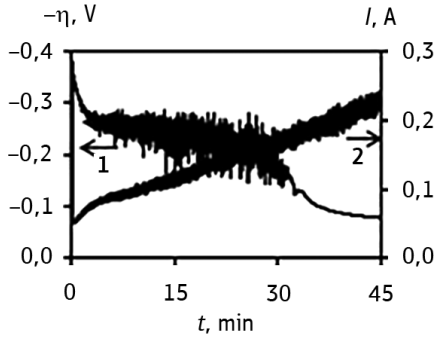

Fig. 2. Change the overvoltage and current in time in galvanostatic (1) and potentiostatic (2) modes

When setting a constant overvoltage throughout the electrolysis maintained a high level of difficulties in delivery of discharging ions. The development of the active surface, on which an electrochemical process is realized, leads to an increase in the amperage in the electrolysis process (Fig. 2, curve 2). As a result, dendrites elongate at a higher and insufficiently time-varying rate in comparison to the electrodeposition at the constant current (Fig. 1).

Differential current output of zinc, which characterizes the ratio of metal and hydrogen recovery processes rates, grows during the electrolysis process in galvanostatic conditions (Fig. 3), that is associated with an increase in the deposit surface and a decrease in the true current density. At the moment of the overvoltage recession and achieving limiting diffusion current density hydrogen ceases to release and the current efficiency tends to unity. Under the conditions of setting the permanent potential the current efficiency changes insufficiently over time and does not exceed 93 % (Fig. 3).

As parameters characterizing the structure of the deposit differential density $d\rho_{oc}$ and differential porosity deposit $d\beta$ have been defined, which were calculated from a change in the metal mass and the overall deposit volume for a fixed period of time. Differential characteristics allow evaluating a change of relevant structural properties of dendrites during the deposition.

As seen in Fig. 4, the deposits have a low density. When setting direct current integrated density of the deposit increases as the recession of active growth of dendrites, and in a constant potential mode it slightly decreases in time. However, the integral density value is an averaged characteristic, so it is less informative.

Differential density allows evaluating change of structural properties of dendrites during the deposition process. According to the thickness of the deposits obtained under potentiostatic conditions, the density changes little (Fig. 5, curve 2), that indicates a uniform structure of the particles. While during electrodeposition of dendrites under galvanostatic conditions, the density increases gradually, and then increases dramatically (Fig. 5, curve 1), that is associated with the intergrowth of separate dendrites branches and a shell formation.

Resulting deposits have high porosity (Fig. 6), which decreases under galvanostatic conditions with cessation of active growth of dendrites (Fig. 6, curve 1) and does not change at a constant potential (Fig. 6, curve 2).

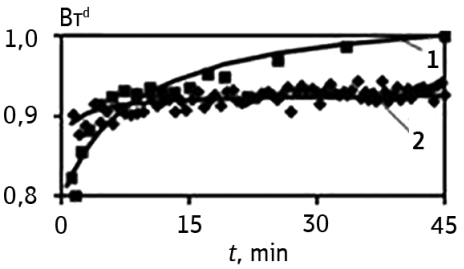

Fig. 3. Change the differential current output in galvanostatic (1) and potentiostatic (2) modes

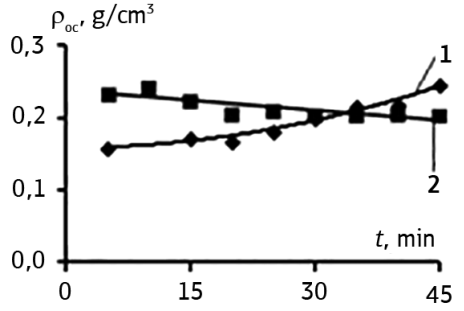

Fig. 4. Change the integral density in time in galvanostatic (1) and potentiostatic (2) modes

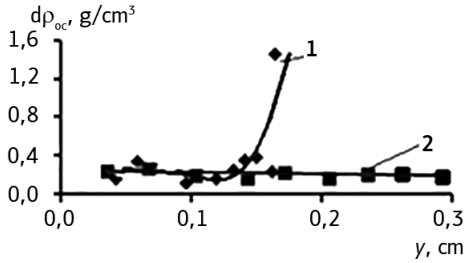

Fig. 5. Change the density over the thickness of dendritic zinc deposits in galvanostatic (1) and potentiostatic (2) modes

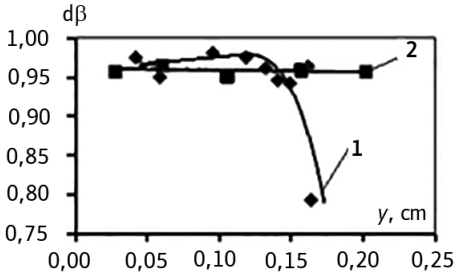

Fig. 6. Change the porosity over the thickness of dendritic zinc deposits in galvanostatic (1) and potentiostatic (2) modes

The studies of morphology of dendritic deposits particles have been conducted using a scanning electron microscope. It is seen in micrographs with a resolution of 20 microns that at the initial stage of electrolysis (10 minutes) the size of certain particles (top radius) slightly differs in deposits obtained in the studied modes

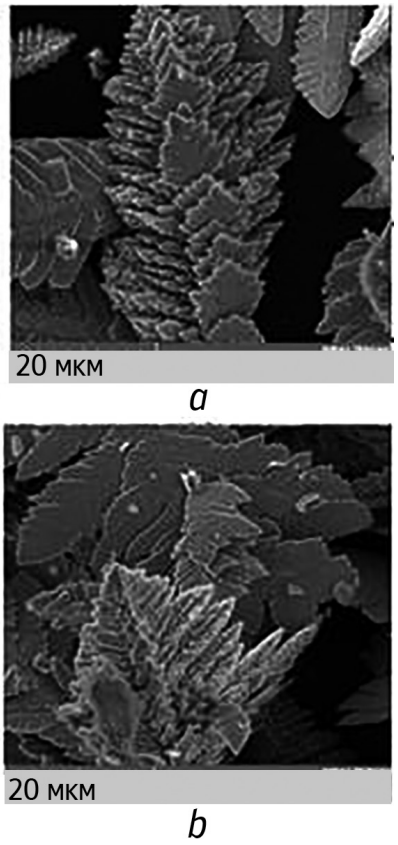

Fig. 7. Micrographs of dendritic zinc deposits obtained in galvanostatic (a) and potentiostatic (b) modes.

(Fig. 7 a, b). The particles are similar both in size and shape resembling fern leaves.

Conclusion

The dynamics of growth of dendritic electrolytic zinc deposits essentially depends on the polarization mode. In galvanostatic conditions there are observed a gradual decrease in the rate of elongation of dendrites and change in the deposit structure from dendritic to compact: density increases and porosity reduces. Whereas in potentiostatic mode dendrites grow at a constant rate, and the loose deposit throughout the thickness has a uniform structure. The study results have been confirmed by deposits micrographs.

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